(21) Yamakawa, H.; Yoshizaki, T. *Macromolecules* **1980**, *13*, 633.
(22) Bohdanecky, M. *Macromolecules* **1983**, *16*, 1483.
(23) Reddy, G. V.; Bohdanecky, M. *Macromolecules* **1987**, *20*, 1393.
(24) Lemieux, R. U.; Purves, C. B. *Can. J. Res., Sect. B.* **1947**, *25B*, 485.
(25) Wirick, M. G.; Waldman, M. H. *J. Appl. Polym. Sci.* **1970**, *14*, 579.
(26) Ambler, M. R.; McIntyre, D. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 589.
(27) Ambler, M. R.; Fetters, L. J.; Kesten, Y. *J. Appl. Polym. Sci.* **1977**, *21*, 2439.
(28) It is, however, possible to obtain fractions with greater polydispersities than that of the parent material in the absence of "cross-fractionation". See: Koningsveld, R. *Pure Appl. Chem.* **1969**, *20*, 271.
(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953; Chapter XIII.
(30) Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; Section IV.
(31) Reference 29, pp 311-13.
(32) Marchessault, R. R.; Sarko, A. *Adv. Carbohydr. Chem.* **1967**, *22*, 445.
(33) Flory, P. J.; Spurr, O. K., Jr.; Carpenter, D. K. *J. Polym. Sci.* **1959**, *27*, 231.
(34) Kamide, K.; Miyazaki, Y. *Polym. J.* **1978**, *10*, 409.
(35) Kamide, K.; Saito, M. *Polym. J.* (*Tokyo*) **1986**, *18*, 569.
(36) Norisuye, T.; Fujita, H. *Polym. J.* (*Tokyo*) **1982**, *14*, 143.
(37) Also, no exact model for chain packing was assumed since insufficient information was available to allow a reliable choice of models to be made. The d spacing at 15.2 Å was assumed to correspond to a first approximation with the chain diameter.
(38) Laivins, G. V.; Gray, D. G. *Macromolecules* **1985**, *18*, 1746.
(39) Laivins, G. V.; Gray, D. G. *Macromolecules* **1985**, *18*, 1753.
(40) Conio, G.; Bianchi, E.; Ciferri, A.; Tealdi, A.; Aden, M. A. *Macromolecules* **1983**, *16*, 1264.
(41) Aden, M. A.; Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A. *Macromolecules* **1984**, *17*, 2010.
(42) Tanner, D. W.; Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 941.
(43) Goebel, K. D.; Harvie, C. E.; Brant, D. A. *Appl. Polym. Symp.* **1976**, *2*, 671.

Fatigue Behavior of Ionomers. 1. Ion Content Effect on Sulfonated Polystyrene Ionomers

Masanori Hara,* Pean-Yue Jar, and J. A. Sauer

Department of Mechanics and Materials Science, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855-0909. *Received December 15, 1987; Revised Manuscript Received April 20, 1988*

ABSTRACT: Fatigue properties of sulfonated polystyrene ionomers were studied as a function of ion content. It was found that the fatigue performance of ionomers decreased with ion content up to ca. 5 mol %. This was attributed to the cross-linking effect of small ionic aggregates (multiplets). The fatigue lifetime increases sharply at ca. 5 mol %, which corresponds to the critical ion content of polystyrene-based ionomers. This increase in fatigue performance is related to the dominant role of large ionic aggregates (clusters). Finally, the fatigue performance of the ionomers increased gradually with ion content, a result attributed to the reinforcing filler effect of the clusters. The fatigue fracture surface morphologies observed by scanning electron microscopy are discussed.

Introduction

It is widely recognized that the introduction of ions into organic polymers modifies their properties dramatically. For example, the glass transition temperature of polyphosphate rises from −10 °C for the nonionic polyacid to +520 °C for the calcium polyphosphate.[1] Many examples of large changes in properties are cited in recent books and reviews.[1-5] Therefore, the introduction of ionic groups into polymer chains has become an interesting and useful approach to modifying the various properties of polymers.

Ionomers are a relatively new class of ion-containing polymers which have ions in concentration up to 10–15 mol %, distributed in nonionic backbone chains. Since the development of ionomers (Surlyn) by DuPont in 1966,[6] ionomers have caught the attention of people in both industry and academia. This is again based on the fact that the incorporation of ions into solid polymers frequently leads to profound changes in properties, such as glass transition temperature and melt viscosity. Much work has been devoted to elucidating the overall structure–property relationships of ionomers. It has been found that the change in properties of ionomers in the solid state is due to the clustering of ion pairs in the medium of low dielectric constant.[1-3] Two types of ionic aggregates are proposed to exist according to ion content:[1] (1) below a certain ion content, multiplets consisting of a small number of ion pairs, which work as physical cross-links, dominate; (2) above that critical ion content, larger aggregates (clusters) consisting not only of ion pairs but also of portions of hydrocarbon chains, which bear many of the characteristics of microphase separation, dominate.

Although much work has been done to elucidate the structure–property relationship of ionomers, most of the properties so far discussed relate to the regions above the glass transition. Such properties as the glass transition temperature, the high-temperature modulus, and the melt viscosity have been determined.[1-3] Little work has been reported in the literature about the glassy state properties, such as yield behavior, impact strength, fatigue behavior, etc., although real use of ionomers as engineering plastics is indeed in the glassy state.

Over recent years there has been a significant increase in interest in the deformation and fracture behavior of glassy polymers.[8,9] One of the reasons is the increasing use of plastics in structural engineering applications. We need to understand the way polymers respond to mechanical deformation, especially, their ultimate properties, to use them for load bearing application. Another reason is that it has become possible recently to achieve some understanding of the deformation/fracture behavior from the microstructure viewpoint.[10]

In this paper, we report the fatigue properties of ionomers. In recent years, considerable attention has been given to the performance of polymers under cyclic loading

0024-9297/88/2221-3183$01.50/0

(fatigue).[11,12] Under cyclic loading, polymers tend to fail at stress levels much lower than they can withstand under monotonic loading. Since the majority of engineering failures involve cyclic loading of one kind or another,[13] it is very important to improve the resistance of polymers to fatigue failure. In order to develop fatigue-resistant polymers systematically, it is essential to elucidate the mechanisms of fatigue failure and correlate them to the microstructure of the polymers.

Deformation and fracture under fatigue loading are closely related to various aspects of the molecular structure of polymers, such as molecular weight, molecular weight distribution, cross-linking, rubber inclusion, etc.[12] Another interesting molecular structure feature that could change the fatigue resistance of polymers is the presence of ionic aggregates.

Recently, we reported preliminary data on the fatigue behavior of sulfonated polystyrene ionomer,[14] which was obtained by a precipitation method:[15] An increase in fatigue lifetime by one decade was observed for ionomer samples which had only 2.8 mol % of ionic groups. However, later detailed studies of these materials[16] revealed the dependence of fatigue performance on sample preparation methods. Two methods used were a precipitation method[15] and a steam stripping method.[17] It was suggested that the first method led to the retention of an excess amount of neutralizing agent (NaOH) that can have a significant effect on the properties of the material. This subject is currently under investigation in this laboratory.

In the present study, we have used the steam stripping method, which does not add any excess amount of NaOH, to elucidate the effect of ion content and ionic aggregates on fatigue properties of ionomers.

Experimental Section

Materials. Lightly sulfonated polystyrene (S-SSA) samples were prepared by solution sulfonation of polystyrene by using the procedure described by Makowski et al.[17] After the reaction was terminated by adding methanol, a steam stripping method was used to recover the polymer. The exact calculated amount of NaOH (dissolved in methanol) was added to neutralize acid groups, followed by steam stripping in the boiling water to recover polymers. Polymers were then washed by methanol and dried under vacuum at 80 °C for at least a week. The ion content of the sample was determined by titration of the acid groups for a small amount of sample taken out from the batch before neutralization. The starting polymer was commercial polystyrene (Mobil PS 1800), which had a number-average molecular weight of 1.41×10^5 and a weight-average molecular weight of 3.09×10^5 ($M_w/M_n = 2.2$).

Specimen. Fatigue samples were prepared by compression molding into 15 cm × 1.6 cm × 1.6 cm rectangular bars. Test specimens were directly machined into hour-glass-shaped round samples with threaded ends (3 in. long, $^1/_5$ in. diameter at the middle, and $^1/_2$ in. diameter at the grip ends). All specimens were carefully polished by using fine grades of emery papers (400, 600, 0000) and finally by lens polishing papers until there was no evidence of surface scratches by microscope observation.

Measurements. Fatigue tests were conducted on an Instron Model 1350 Servohydraulic testing machine at room temperature. A sinusoidal waveform was used with a frequency of 5.0 Hz for tension–compression cycling. In these tests, the maximum applied load was 50 lb, corresponding to a stress amplitude of 11 MPa.

The fracture surfaces were examined by a scanning electron microscope (SEM) (Etec) after the surfaces were coated with a thin layer of gold.

A light reflection method was used to determine the onset of initiation of surface defect zones.[18] The reflected light intensity from the specimen was monitored by the recorder connected to a photodetector. The number of cycles of initiation, N_i, is defined as a number of cycles where the output voltage starts to increase. Also, the lifetime of the specimen, N_f, was defined as the number of cycles to sample failure. Data points are average value of N_f and N_i for several samples.

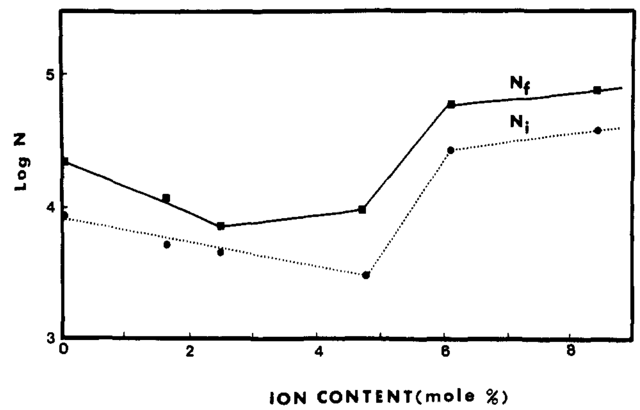

Figure 1. Effect of ion content on cycles to fracture, N_f (solid line), and cycles to damage initiation, N_i (dotted line), for ionomer samples subject to a stress amplitude of 11 MPa.

Results and Discussion

Figure 1 shows the average fatigue lifetime (cycles to fracture), N_f, and the cycles for the initiation of surface defect zones, N_i, as a function of ion content. It is seen that fatigue performance decreases with increasing ion content up to critical ion content (ca. 5 mol %). At around this ion content, the fatigue lifetime jumps by 1 order of magnitude or so. Then, the fatigue performance increases gradually above this ion content.

The most plausible interpretation of these data is that they result essentially from a transition from multiplet to cluster formation as ion content passes through the critical range.[1] At low ion content, the small ionic aggregates (multiplets) dominate, and these act as ionic cross-links. Eisenberg and Navratil[19] reported that for styrene–methacrylic acid ionomers (S-MAA-Na), the position of the high inflection point in the stress relaxation master curve could be predicted from the classical theory of rubber elasticity, assuming that each ion pair is incorporated in a cross-link up to ca. 6 mol %. Above 6 mol %, the deviation of data points from the calculated curve is very large. For sulfonated polystyrene ionomers (S-SSA-Na), the inflection point in stress relaxation master curves[20] and the rubbery plateau region in dynamic mechanical data[21] seemed to follow the classical rubber theory at low ion content. Therefore, it is generally concluded that polystyrene-based ionomers with low ion content show a crosslinking effect due to multiplet formation.

It is well-known that the fatigue performance decreases with increasing cross-link density.[11] In fracture mechanics type of experiments with notched specimen, it was reported that for cross-linked PMMA, da/dN vs ΔK curves shift to the left with increasing cross-linking; i.e., the fatigue crack propagation rate increases with cross-linking. Here, a is the length of the crack and ΔK is the stress intensity factor range. Similar results were obtained for epoxy resins.[22] Herzberg and Manson suggested that there existed a correlation between molecular chain mobility and fatigue resistance; cross-linked resins, possessing a tightly constrained structure and intolerant of plastic deformation, lead to an accelerated fatigue growth rate. Moreover, due to the constraints imposed on polymer chains, less energy is dissipated, and the material behaves in a more brittle manner. This is indeed our experience for ionomer samples with ion content less than the critical ion content (ca. 5 mol %).

At higher ion contents, the larger ionic aggregates (clusters) play a dominant role in determing the physical

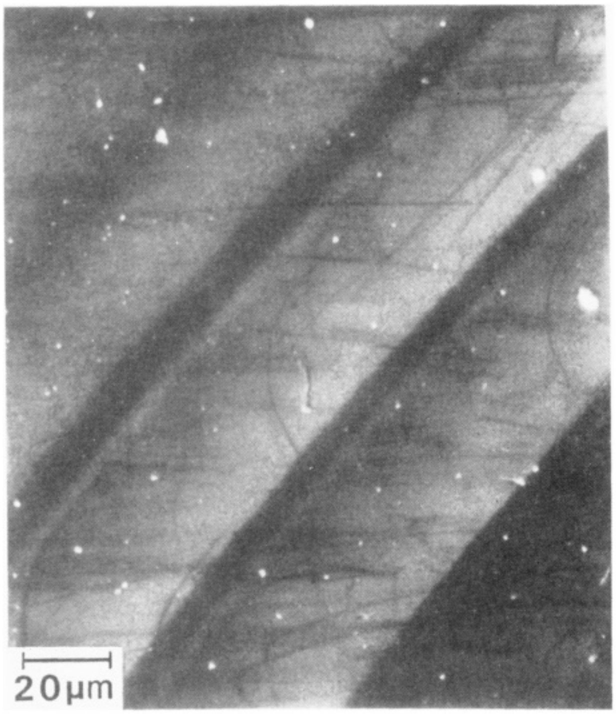

Figure 2. Fatigue fracture surface of polystyrene tested at a stress amplitude of 11 MPa and at 5 Hz.

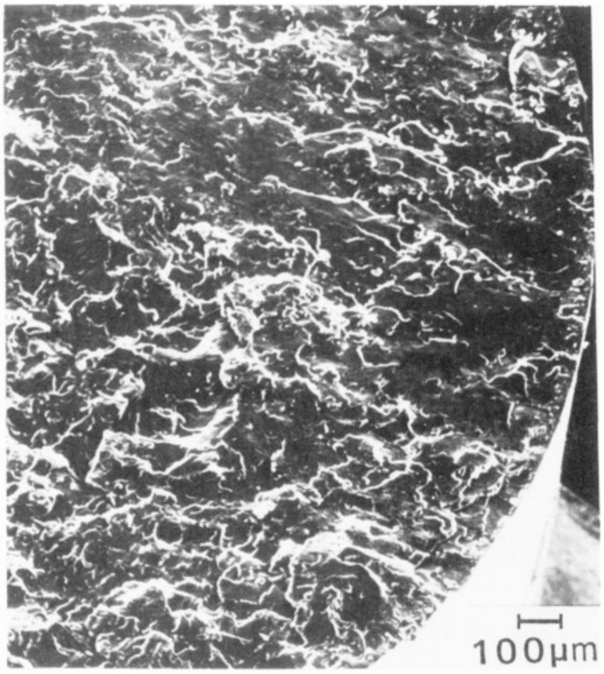

Figure 3. Fatigue fracture surface of ionomer sample with 2.5 mol % ion content.

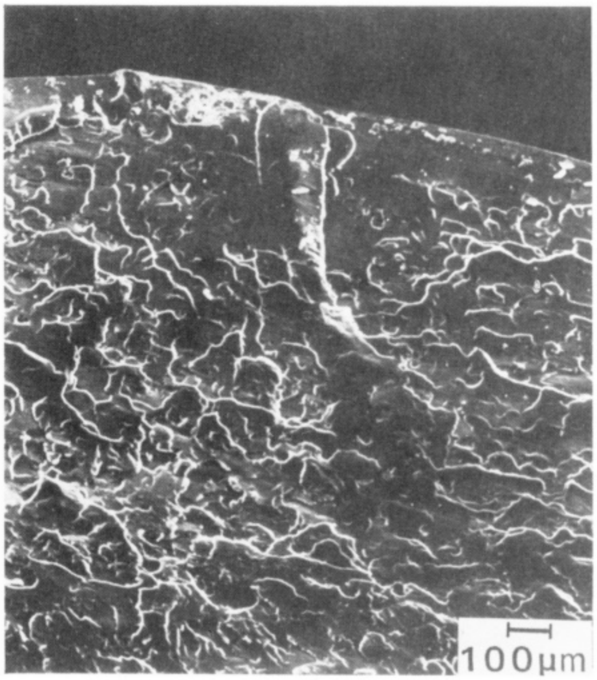

Figure 4. Fatigue fracture surface of ionomer sample with 4.8 mol % ion content.

Figure 5. Fatigue fracture surface of ionomer sample with 6.1 mol % ion content.

properties. From other measurements on polystyrene-based ionomers, the critical ion content was estimated as 4–6 mol %.[1,23] Our data are in good agreement with these values. Above this critical ion content, the clusters appear to act as reinforcing fillers and contribute to an increase in fatigue performance. More recent data by Raman spectroscopy[24] and dielectric[25] measurements suggest that the transition at critical ion content is not the all multiplets to all clusters transition; rather the change is more gradual in that the amount of multiplets saturate with increasing ion conent, while that of clusters increases constantly. Therefore, the crticial ion content is the point where the effect of clusters dominate to that of multiplets on physical properties including mechanical properties. This interpretation of critical ion content is consistent with our data.

Figures 2–6 show SEM pictures of the fracture surface morphology of some of the fracture samples under fatigue loading. For the sample with low ion content (2.5 and 4.8 mol %), quite rough textures are seen (Figures 3 and 4). This is in contrast to results obtained on the PS samples (Figure 2), which show a smooth mirror region, with a series of discontinuous crack growth (DCG) bands representing crack propagation through essentially a single craze that successively develops from each crack tip position and a rough region representing the later stages of catastrophic crack propagation.[11,12] In the mirror region, the width of the DCG bands, which represent the craze length or the plastic zone size at the crack tip prior to crack jumping through the fatigue-damaged craze, increases with an in-

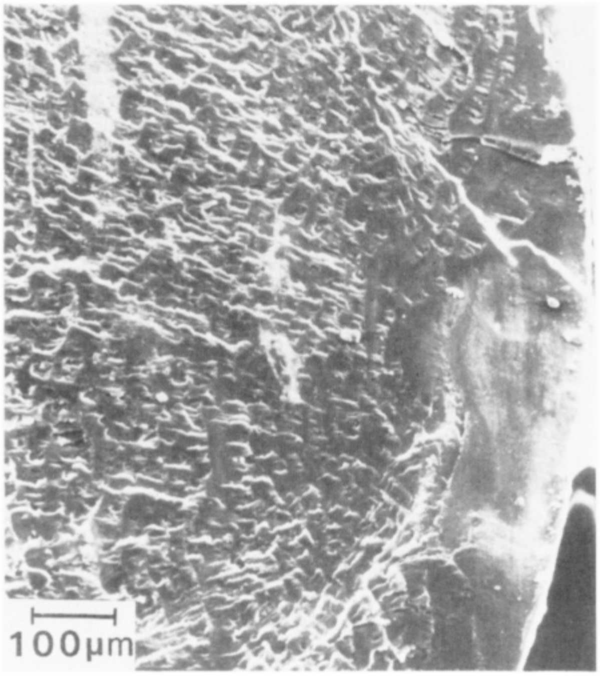

Figure 6. Fatigue fracture surface of ionomer sample with 8.5 mol % ion content.

crease in crack length. The rough textures in the ionomer samples with low ion contents may arise from crack propagation through unstable small crazes. Samples of low ion content subject to simple tension also show loss of craze stability and earlier craze breakdown.[26,27] However, in samples with higher ion content (6.1 and 8.5 mol %), craze stability appears to increase and concentric bands surrounding the fracture initiation sites appear again (Figures 5 and 6). These bands are not as well-defined as DCG bands in PS, but this may be a result of some localized shear deformation as well as crazing. It is known that under simple tension these samples show both crazing and localized shear deformation[26,27] and that localized shear yielding is expected to suppress craze growth and stabilize crazes.[9] This behavior seems to be consistent with our fatigue data.

Conclusion

Fatigue properties of sulfonated polystyrene ionomers were studied as a function of ion content. It is found that the fatigue performance of ionomers decreases with increasing ion content up to ca. 5 mol %. This is attributed to the cross-linking effect of small ionic aggregates (multiplets). The cross-linking decreases chain mobility, dissipates less energy, and makes the ionomer more brittle. The craze stability appears to decrease with increasing ion content, leading to a rather textured fracture surface morphology. The fatigue lifetime increases sharply at ca. 5 mol %, which appears to correspond to the critical ion content of polystyrene-based ionomers. Therefore, this increase in fatigue performance is related to the dominant role of large ionic aggregates (clusters). Finally, the fatigue performance of these ionomers increases gradually with ion content, which may be attributed to a reinforcing filler effect of the clusters. Also, a regained craze stability is seen in the appearance of DCG type concentric bands on the fatigue fracture surface.

The above results from fatigue studies of ionomers are consistent with results on deformation and fracture behavior of ionomers obtained under simple tension. These results will be reported soon.[27] Although explanation of results by the concept of ionic cross-linking seems to be very plausible for ionomers with low ion content, the specific role of ionic clusters for ionomers with high ion content is not clear at this stage. The detailed mechanism of the reinforcing filler effect of clusters is currently under investigation.

Acknowledgment. We thank Mobil Chemical Co, Edison, NJ, for kindly supplying the polystyrene samples. Financial support from the Rutgers Research Council is gratefully acknowledged. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

(1) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.
(2) MacKnight, W. J.; Earnest, T. R. *Macromol. Rev.* **1981**, *16*, 41.
(3) Wilson, A. D., Prosser, H. J., Eds. *Development in Ionic Polymers*; Applied Science: New York, 1983.
(4) Eisenberg, A., Bailey, F. E., Eds. *Coulombic Interactions in Macromolecular Systems*; ACS Symposium Series #301; American Chemical Society: Washington, DC, 1986.
(5) Pineri, M., Eisenberg, A., Eds. *Structure and Properties of Ionomers*; NATO ASI Series; Plenum: New York, 1987.
(6) Rees, R. W. U.S. Patent 3 264 272, 1966, assigned to E. I. du Pont de Nemours & Co.
(7) Rosen, B., Ed. *Fracture Processes in Polymeric Solids*; Interscience: New York, 1964.
(8) Andrews, E. H., Ed. *Developments in Polymer Fracture*; Applied Science: New York, 1979.
(9) Kinloch, A. J.; Young, R. J. *Fracture Behavior of Polymers*; Applied Science: New York, 1983.
(10) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *52/53*, 1.
(11) Hertzberg, R. W.; Manson, J. A. *Fatigue of Engineering Plastics*; Academic: New York, 1980.
(12) Sauer, J. A.; Richardson, G. C. *Int. J. Fract.* **1980**, *16*, 499.
(13) Hertzberg, R. W. *Deformation and Fracture Mechanics of Engineering Materials*; Wiley: New York, 1983.
(14) Hara, M.; Jar, P. *Polym. Commun.* **1987**, *28*, 52.
(15) Lundberg, R. D.; Makowski, H. S. *Adv. Chem. Ser.* **1980**, *No. 187*, 21.
(16) Jar, P.; Sauer, J. A.; Hara, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(2), 367.
(17) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3 870 841, 1975, assigned to Exxon Research and Engineering Co.
(18) Sauer, J. A.; Chen, C. C. *Adv. Polym. Sci.* **1983**, *52/53*, 169.
(19) Eisenberg, A.; Navratil, M. *Macromolecules* **1973**, *6*, 604.
(20) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641.
(21) Lefelar, J. A.; Weiss, R. A. *Macromolecules* **1984**, *17*, 1145.
(22) Kim, S. L.; Skibo, M. D.; Manson, J. A.; Hertzberg, R. W.; Janiszewski, J. *Polym. Eng. Sci.* **1978**, *18*, 1093.
(23) Bazuin, C. G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271.
(24) Neppel, A.; Butler, I. S.; Brockman, N.; Eisenberg, A. *J. Macromol. Sci., Phys.* **1981**, *B19*, 61.
(25) Hodge, I. M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 283.
(26) Hara, M.; Jar, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(2), 365.
(27) Hara, M.; Jar, P. *Macromolecules*, in press.